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click for updatesCite this: *Chem. Sci.*, 2015, 6, 3003**Ru(II)–Re(I) binuclear photocatalysts connected by –CH<sub>2</sub>XCH<sub>2</sub>– (X = O, S, CH<sub>2</sub>) for CO<sub>2</sub> reduction†**Eishiro Kato,<sup>a</sup> Hiroyuki Takeda,<sup>ab</sup> Kazuhide Koike,<sup>bc</sup> Kei Ohkubo<sup>a</sup>  
and Osamu Ishitani<sup>\*ab</sup>

We developed Ru(II)–Re(I) supramolecular photocatalysts in which each metal complex unit is connected by a –CH<sub>2</sub>XCH<sub>2</sub>– (X = O, S, CH<sub>2</sub>) chain. The photocatalyst with X = O exhibited the best photocatalytic efficiency for CO<sub>2</sub> reduction in the reported systems using a NAD(P)H model compound as an electron donor because the introduced oxygen atom strengthened the oxidation power of the Ru photosensitizer unit in the excited state and accelerated electron transfer from the one-electron-reduced Ru photosensitizer unit to the Re catalyst unit. In contrast, the catalytic ability of the photocatalyst with X = S rapidly decreased during irradiation because the supramolecular structure split into mononuclear complexes. A detailed mechanism for the efficient photocatalytic reaction involving these supramolecular photocatalysts was investigated for the first time.

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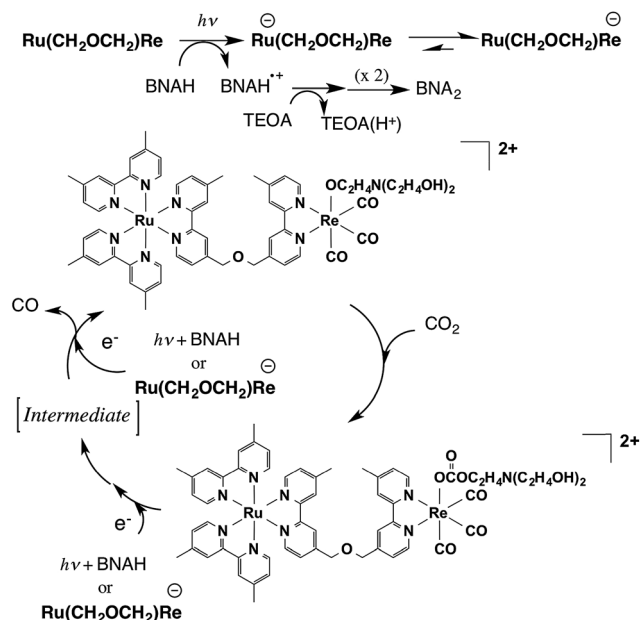
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**Introduction**

The conversion of CO<sub>2</sub> into high-energy compounds using solar energy is a potential technology for addressing both the problem of global warming and the shortage of fossil fuel resources.<sup>1</sup> Some transition metal complexes can broadly absorb visible light and function as redox photosensitizers, which drive one-electron-transfer reactions.<sup>2</sup> However, because the reduction of CO<sub>2</sub> to stable compounds requires multi-electron insertion into CO<sub>2</sub>, a catalyst is also required for photocatalytic CO<sub>2</sub> reduction systems.<sup>3</sup> Electrochemical catalysts for CO<sub>2</sub> reduction using transition metal complexes<sup>5</sup> or a pyridinium cation<sup>6</sup> have been developed, and some of them have been applied for photocatalytic systems with redox photosensitizers.<sup>7</sup> As typical examples, mixed systems consisting of [Ru(N<sup>^</sup>N)<sub>3</sub>]<sup>2+</sup> (N<sup>^</sup>N = diimine ligand) as a photosensitizer and

Co, Ni, and Ru complexes as a catalyst have been reported to photocatalyze CO<sub>2</sub> reduction to CO and/or HCOOH using visible light.<sup>4</sup>

We have developed supramolecular photocatalysts with a Ru(II) photosensitizer and a Re(I) catalyst connected to each other *via* a bridging ligand consisting of two diimine moieties connected with an alkyl chain,<sup>8</sup> *e.g.*, Ru(CH<sub>2</sub>CH<sub>2</sub>)Re (Chart 1): the quantum yield ( $\Phi_{\text{CO}}$ ) and the turnover number (TON<sub>CO</sub>) of



**Scheme 1** Partial reaction mechanism of photocatalytic CO<sub>2</sub> reduction by Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re.

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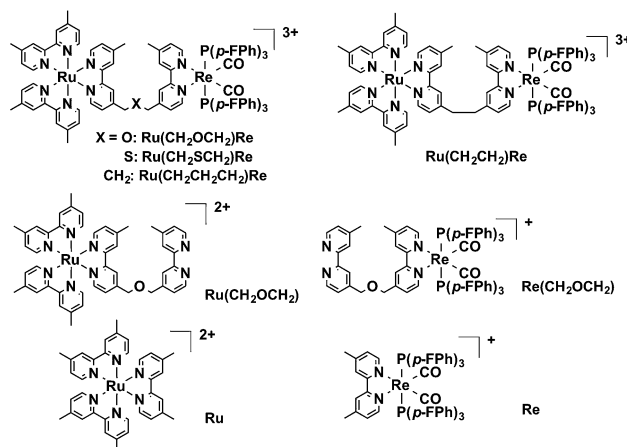
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† Electronic supplementary information (ESI) available: Stern–Volmer plots of the dyad; UV-vis spectra of the OERs of Ru and Re; UV-vis spectral changes during the photocatalytic reaction; ESI-MS spectrum of the SEC peak at 36.1 min after the 120 min photocatalytic reaction using Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(X) (X = <sup>−</sup>OC<sub>2</sub>H<sub>4</sub>N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub> or <sup>−</sup>OC(O)OC<sub>2</sub>H<sub>4</sub>N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub>); Stern–Volmer plots for Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(X) (X = <sup>−</sup>OC(O)OC<sub>2</sub>H<sub>4</sub>N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub>); changes of SEC chromatograms, ESI-MS spectra, and IR spectra during the photocatalytic reaction using Ru(CH<sub>2</sub>CH<sub>2</sub>)Re; changes of a ESI-MS spectrum after the photocatalytic reaction; ESI-MS spectra of the SEC peak at 36.5 min and 37.8 min after the 120 min photocatalytic reaction using Ru(CH<sub>2</sub>SCH<sub>2</sub>)Re. See DOI: 10.1039/c4sc03710c



In this report, new Ru(II)–Re(I) diads with bridging ligands constructed of two diimines connected by  $-\text{CH}_2\text{OCH}_2-$  or  $-\text{CH}_2\text{SCH}_2-$  were synthesized and investigated as photocatalysts with enhanced oxidation power; their enhanced oxidation power stems from the greater electronegativity of the bridging ligands' oxygen and sulfur atoms compared to that of the central carbon atom in the alkyl chains such as  $-\text{CH}_2\text{CH}_2\text{CH}_2-$  (Chart 1). The diad with the  $-\text{CH}_2\text{OCH}_2-$  chain exhibited the best performance



**Chart 1** Structures and abbreviations of the metal complexes.

as a supramolecular catalyst for CO<sub>2</sub> reduction using BNAH as the reductant. A detailed mechanism of CO<sub>2</sub> reduction using the Ru-Re diads is also reported for the first time.

## Results and discussion

The diads were synthesized by the following method: the reaction of  $[(\text{dmb})_2\text{RuCl}_2]^{2+}$  ( $\text{dmb} = 4,4'$ -dimethyl-2,2'-bipyridine) and the bridging ligand gave  $\text{Ru}(\text{CH}_2\text{XCH}_2)$  ( $\text{X} = \text{O}, \text{S}, \text{CH}_2$ ) with a bridging ligand with a non-coordinated diimine moiety;  $\text{Ru}(\text{CH}_2\text{XCH}_2)$  was subsequently reacted with  $[\text{Re}(\text{CO})_3\{\text{P}(\text{p-FPh})_3\}_2(\text{OTf})]$  to give  $\text{Ru}(\text{CH}_2\text{XCH}_2)\text{Re}$  in 8–32% yield calculated on the basis of the amount of  $[(\text{dmb})_2\text{RuCl}_2]^{2+}$  used.

Fig. 1a shows the UV-vis absorption spectra of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** and its model mononuclear complexes (**Ru(CH<sub>2</sub>OCH<sub>2</sub>)** and **Re(CH<sub>2</sub>OCH<sub>2</sub>)**), and Fig. 1b shows those of **Ru(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Re** and its models (**Ru** and **Re**). The spectra of both diads are approximately consistent with the summation spectra of their model complexes, as shown by the dotted lines in the figures. The results indicate that no strong electronic interaction occurs between the Ru and Re units in the ground states of both diads. The broad absorption at 400–550 nm is assignable to metal-to-

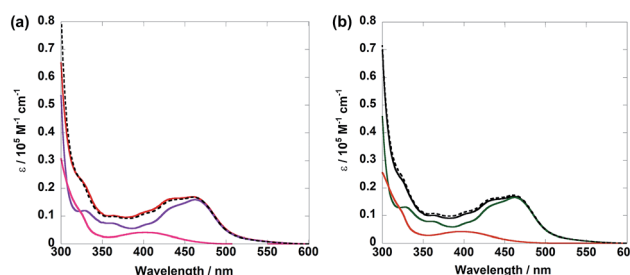
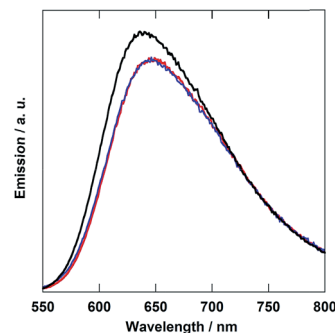


Fig. 1 UV-vis absorption spectra of (a) Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re (red), Ru(CH<sub>2</sub>OCH<sub>2</sub>) (purple), and Re(CH<sub>2</sub>OCH<sub>2</sub>) (pink), and (b) Ru(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Re (black), Ru (green), and Re (red). The dotted lines show the 1:1 summation spectrum of (a) Ru(CH<sub>2</sub>OCH<sub>2</sub>) and Re(CH<sub>2</sub>OCH<sub>2</sub>) and (b) Ru and Re. Dimethylformamide (DMF) was used as the solvent.

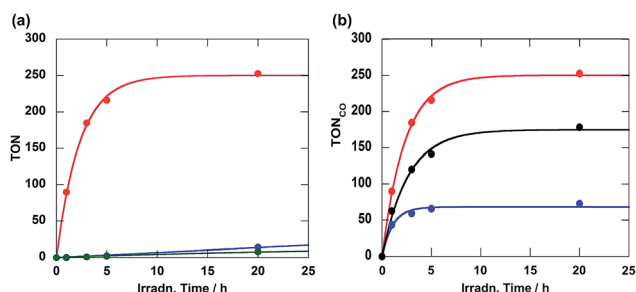
Fig. 3 shows the emission spectra of the diads. In all cases, broad emission from the  $^3\text{MLCT}$  excited state of the Ru unit was observed. The emission maxima of both  $\text{Ru}(\text{CH}_2\text{OCH}_2)\text{Re}$  and  $\text{Ru}(\text{CH}_2\text{SCH}_2)\text{Re}$  were red-shifted by 10 nm compared to that of  $\text{Ru}(\text{CH}_2\text{CH}_2\text{CH}_2)\text{Re}$ . The emission quantum yields ( $\Phi_{\text{em}}$ ) and emission lifetimes ( $\tau_{\text{em}}$ ) of  $\text{Ru}(\text{CH}_2\text{OCH}_2)\text{Re}$  and  $\text{Ru}(\text{CH}_2\text{SCH}_2)\text{Re}$  decreased compared to those of  $\text{Ru}(\text{CH}_2\text{CH}_2\text{CH}_2)\text{Re}$  according to the energy-gap law (Table 1). These emission properties of the Ru units in both  $\text{Ru}(\text{CH}_2\text{OCH}_2)\text{Re}$  and  $\text{Ru}(\text{CH}_2\text{CH}_2\text{CH}_2)\text{Re}$  were very similar to those of their model mononuclear complexes, *i.e.*,  $\text{Ru}(\text{CH}_2\text{OCH}_2)$  and  $\text{Ru}$ , respectively (Table 1). These similarities strongly suggest that the difference between the emission properties of  $\text{Ru}(\text{CH}_2\text{OCH}_2)\text{Re}$  and  $\text{Ru}(\text{CH}_2\text{CH}_2\text{CH}_2)\text{Re}$  was mainly caused by the introduction of the oxygen atom into the bridging



**Fig. 3** The emission spectra of Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re (red), Ru(CH<sub>2</sub>SCH<sub>2</sub>)Re (blue), and Ru(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Re (black) collected at 25 °C in DMF; the spectra are normalized to the absorbance of the solutions at  $\lambda_{\text{excitation}} = 456$  nm.

ligand; thus, introduction of the Re unit into the opposite side did not strongly affect the emission properties in either case. This result also suggests that intramolecular quenching of the <sup>3</sup>MLCT of the Ru unit by electron and/or energy transfer to the Re unit did not proceed or proceeded with very low efficiency.

Emission from the Ru units in all of the diads was reductively quenched by BNAH, and the Stern–Volmer plots of the emission quenching exhibited good linearity (Fig. S1, ESI†). Table 1 summarizes the quenching rate constants of the emission from the Ru units ( $k_q$ ) and the quenching fractions with 0.1 M BNAH ( $\eta_q$ ). Under the photocatalytic reaction conditions, the  $\eta_q$  values of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** and **Ru(CH<sub>2</sub>SCH<sub>2</sub>)Re** were approximately 10% higher than that of **Ru(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Re**. This result strongly suggests that the oxidizing powers of the excited Ru units in **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** and **Ru(CH<sub>2</sub>SCH<sub>2</sub>)Re** were improved compared with that of the excited Ru units in **Ru(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Re**, likely because of the high electronegativities of the heteroatoms introduced into the bridging ligands. The increased quenching fraction should be partly responsible for improving the photocatalytic activity of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re**. However, the quenching fraction of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** increased only 1.2-fold compared with that of **Ru(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Re**, whereas the quantum yield of CO formation in the case of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** increased by 1.7 times compared with that in the case of **Ru(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Re**. Other factors likely contribute to the improvement of the photocatalytic activity of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re**. In addition, both the  $\Phi_{\text{CO}}$  and  $\text{TON}_{\text{CO}}$  in the case of **Ru(CH<sub>2</sub>SCH<sub>2</sub>)Re** were lower compared to those in the case of **Ru(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Re**, even though the  $\eta_q$  of **Ru(CH<sub>2</sub>SCH<sub>2</sub>)Re** was greater than that of **Ru(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Re**.



**Fig. 2** (a) Turnover number of  $\text{Ru}(\text{CH}_2\text{OCH}_2)\text{Re}$  for CO (red),  $\text{HCOOH}$  (green), and  $\text{H}_2$  (blue) formation and (b) those of  $\text{Ru}(\text{CH}_2\text{OCH}_2)\text{Re}$  (red),  $\text{Ru}(\text{CH}_2\text{SCH}_2)\text{Re}$  (black), and  $\text{Ru}(\text{CH}_2\text{CH}_2\text{CH}_2)\text{Re}$  (blue) for CO formation as a function of irradiation time. DMF–TEOA (5 : 1) solutions containing 0.05 mM of the diad and 0.1 M of BNAH were irradiated at  $\lambda > 500$  nm under a  $\text{CO}_2$  atmosphere.

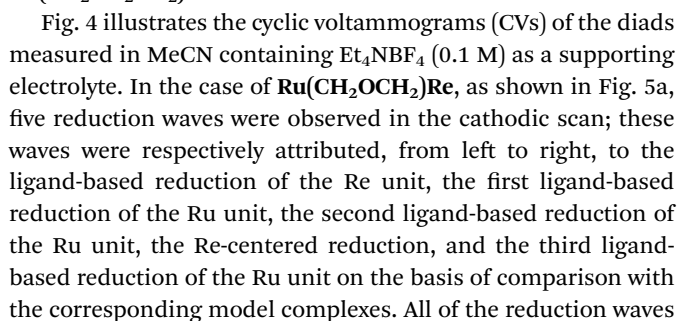


Table 1 Emission properties of the metal complexes and quenching rates of the emission by BNAH<sup>a</sup>

Complex	$\lambda_{\text{em}}^a/\text{nm}$	$\Phi_{\text{em}}^a$	$\tau_{\text{em}}^a/\text{ns}$	$k_q\tau^{b,c}/\text{M}^{-1}\text{s}^{-1}$	$k_q/10^7\text{M}^{-1}$	$\eta_q^d$
<b>Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re</b>	649	0.087	735	42.1	5.73	0.82
<b>Ru(CH<sub>2</sub>SCH<sub>2</sub>)Re</b>	649	0.087	734	36.3	4.95	0.78
<b>Ru(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Re</b>	639	0.097	761	21.0	2.76	0.67
<b>Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(X)</b> X = <sup>−</sup> OC(O)OC <sub>2</sub> H <sub>4</sub> N(C <sub>2</sub> H <sub>4</sub> OH) <sub>2</sub>	645	0.119 <sup>b</sup>	724 <sup>b</sup>	14.0	1.92	0.58
<b>Ru</b>	639	0.086	760	—	—	—
<b>Ru(CH<sub>2</sub>OCH<sub>2</sub>)</b>	649	0.092	747	—	—	—

<sup>a</sup> DMF was used as the solvent, and the excitation wavelength was 456 nm. <sup>b</sup> DMF-TEOA (5 : 1 v/v) was used as the solvent. <sup>c</sup> The excitation wavelength was 520 nm. <sup>d</sup> Quenching fraction with 0.1 M BNAH,  $\eta_q = 1 - 1/(1 + k_q\tau[\text{BNAH}])$ .



Fig. 4 Cyclic voltammograms of (a) **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** (red) and **Ru(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Re** (black), and (b) **Ru(CH<sub>2</sub>SCH<sub>2</sub>)Re** (blue) and **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** (red) measured in MeCN containing Et<sub>4</sub>NBF<sub>4</sub> (0.1 M) as the supporting electrolyte.



Fig. 5 *In situ* differential UV-vis absorption spectra of the reaction solutions before and after irradiation: (a) **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re**, where the irradiation time was 840–1080 s at intervals of 60 s; (b) **Ru(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Re**, where the irradiation time was 2640–2760 s at intervals of 30 s. DMF-TEOA (5 : 1) solutions containing BNAH (0.1 M) and the complex (0.3 mM) were irradiated under a CO<sub>2</sub> atmosphere at  $\lambda = 480\text{ nm}$  with a light intensity of  $3.2 \times 10^{-9}\text{ einsteins}^{-1}$ .

except for the Re-centered reduction were reversible. In the anodic scan, two oxidation waves were observed, the reversible wave at  $E_{1/2} = 0.82\text{ V}$  and the irreversible wave at  $E_p = 1.21\text{ V}$  were attributed to the Ru-centered (Ru(II)/Ru(III)) and the Re-centered oxidation (Re(I)/Re(II)), respectively.

All redox waves in the CV of **Ru(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Re** were similarly observed but negatively shifted compared to those of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** (Fig. 4a). In the case of **Ru(CH<sub>2</sub>SCH<sub>2</sub>)Re**, however, the ligand-based reduction of the Re unit was irreversible and the Re-centered reduction wave could not be identified (Fig. 4b). This result suggests that the one-electron-reduced species (OERs) of **Ru(CH<sub>2</sub>SCH<sub>2</sub>)Re** was less stable than the corresponding OERs of the other diads. The first reduction waves of the Re units in both **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** and **Ru(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Re** were observed at potentials similar to those of the corresponding model complexes, *i.e.*, **Re(CH<sub>2</sub>OCH<sub>2</sub>)** and **Re** (Table 2). This observation also indicates that the Ru unit did not exert a strong electronic effect on the Re units through the bridging ligand. Therefore, the positive shifts of the redox potentials of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** compared to those of **Ru(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Re**, as described above, are attributable mainly to the electron-withdrawing ability of the oxygen atom in the bridging ligand, which lowers the HOMO and LUMO energies of the Ru and Re units.

The first reduction of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)** was observed at a potential 20 mV more positive than that of **Ru**; however, the first reduction of **Re(CH<sub>2</sub>OCH<sub>2</sub>)** was 50 mV more positive than that of **Re** (Table 2). This discrepancy indicates that the introduction of an oxygen atom into the bridging ligand more strongly affected the LUMO energy of the Re unit than that of the Ru unit and that, in the case of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re**, the driving force of intramolecular electron transfer from the OERs of the Ru unit to the Re unit was greater than that of **Ru(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Re**.

These results are consistent with the differences between the UV-vis absorption spectra of the solutions during the photocatalytic reactions in the presence of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** and **Ru(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Re** (Fig. 5). In the case of **Ru(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Re**, a relatively sharp absorption band with a maximum at 520 nm appeared during irradiation (Fig. 5a). The corresponding absorption band of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** was broader, with relatively stronger absorption at wavelengths longer than  $\sim 560\text{ nm}$  (Fig. 5b). Both spectra were fitted by a linear combination of the absorption spectra of the OERs of **Ru** and **Re**, which were obtained by the flow electrolysis method (Fig. S2, ESI†). Using these data, we calculated the ratios of the OERs between the Ru and Re units to be 1 : 1.3 in the case of **Ru(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Re**, and 1 : 9.3 in the case of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** (Fig. S3, ESI†). These results strongly indicate that the added electron was more

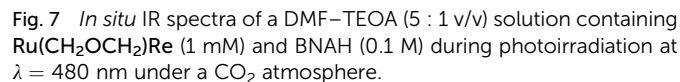
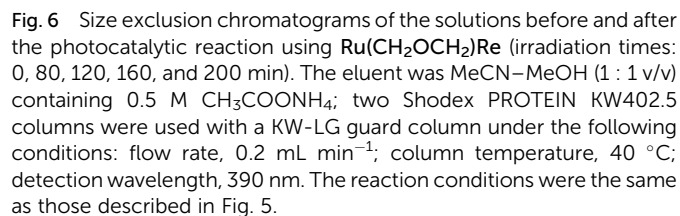




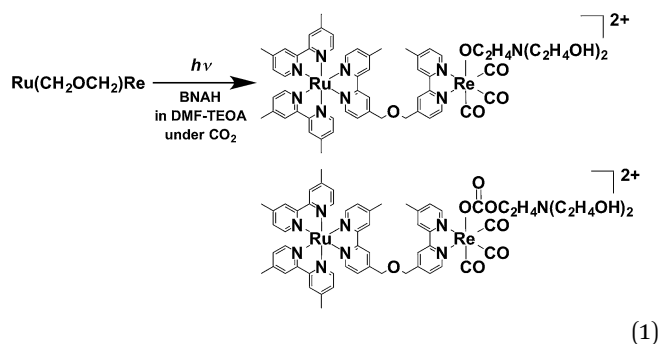
<sup>a</sup> Peak potential of the irreversible wave. <sup>b</sup> The wave was not identified. <sup>c</sup> From ref. 8e.

Fig. 6 illustrates size-exclusion chromatograms of the reaction solution in the case of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re**. Before irradiation, only a single peak attributed to **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** was observed at 34.9 min. The irradiation induced a decrease in the intensity of the peak of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** with the appearance of a new peak at 36.1 min; after 120 min of irradiation, a photostationary state, where the ratio of the peak areas was approximately 3 : 1, was observed. The electrospray ionization (ESI) mass spectra of the eluents collected at 36.1 min showed a peak attributable to  $[(\text{dmb})_2\text{Ru}(\text{CH}_2\text{OCH}_2)\text{Re}(\text{CO})_3(\text{CH}_3\text{COO}^-)]^{2+}$ , whose  $\text{CH}_3\text{COO}^-$  group likely originated from the eluent (MeCN–MeOH (1 : 1 v/v) containing 0.05 M  $\text{CH}_3\text{COONH}_4$ ) at  $m/z = 591$  (Fig. S4, ESI<sup>†</sup>). This result strongly suggests that the Re unit in some **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** complexes was converted into a tricarbonyl complex, *i.e.*, *fac*-[Re(N<sup>^</sup>N)(CO)<sub>3</sub>(L)] (N<sup>^</sup>N = diimine ligand, L = monodentate ligand), during the first stage of the photocatalytic reaction.

Fig. 7 shows *in situ* IR spectral changes of a solution during the photocatalytic reaction. The concentration of the diad was greater than that used in the case of Fig. 6 because of the lower sensitivity of the IR spectrometer compared to that of the size exclusion chromatograph. Immediately after the irradiation was initiated, the CO-stretching bands corresponding to the Re unit of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** ( $\nu_{\text{CO}} = 1938$  and  $1868\text{ cm}^{-1}$ ) decreased in intensity, whereas a pair of bands of the corresponding OERs ( $\nu_{\text{CO}} = 1909$  and  $1836\text{ cm}^{-1}$ ) increased in intensity.<sup>10</sup> Further irradiation resulted in the formation of new bands attributable to two kinds of diads with a Re tricarbonyl unit ( $\nu_{\text{CO}} = 2018$ ,  $2006$ , and  $\sim 1890\text{ cm}^{-1}$ ; other  $\nu_{\text{CO}}$  bands associated with these species should be observed, but they were overlapped by the bands of other species). These species were identified as diads with two types of the Re units: *fac*-[Re(N<sup>^</sup>N)(CO)<sub>3</sub>OC<sub>2</sub>H<sub>4</sub>N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub>]} with a deprotonated TEOA ligand, and its CO<sub>2</sub>-inserted product, *fac*-[Re(N<sup>^</sup>N)(CO)<sub>3</sub>OC(O)OC<sub>2</sub>H<sub>4</sub>N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub>]}, where both TEOA and CO<sub>2</sub> molecules are captured to form a carbonate ester ligand. These structural assignments are based on the similarities of these species to the corresponding Re mononuclear complexes, *i.e.*, *fac*-[Re(bpy)(CO)<sub>3</sub>OC<sub>2</sub>H<sub>4</sub>N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub>]} ( $\nu_{\text{CO}} = 2006$ ,  $1897$ ,  $1881\text{ cm}^{-1}$ ) and *fac*-[Re(bpy)(CO)<sub>3</sub>{OC(O)OC<sub>2</sub>H<sub>4</sub>N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub>]} ( $\nu_{\text{CO}} = 2020$ ,  $1915$ ,  $1892\text{ cm}^{-1}$ ) (bpy = 2,2'-bipyridine), reported in our previous paper.<sup>11</sup> As described below, the IR spectra of authentic samples of the diads with either a <sup>-</sup>OC<sub>2</sub>H<sub>4</sub>N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub> or a <sup>-</sup>OC(O)OC<sub>2</sub>H<sub>4</sub>N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub> ligand, *i.e.*, **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(X)** (X = <sup>-</sup>OC<sub>2</sub>H<sub>4</sub>N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub>



or  $^-OC(O)OC_2H_4N(C_2H_4OH)_2$ ) also showed similar CO-stretching bands (Fig. S5, ESI<sup>†</sup>). These results strongly indicate that **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** was partially converted into **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(X)** in the first stage of the photocatalytic reaction (eqn (1)).

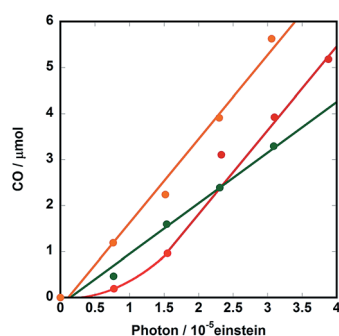


Further irradiation resulted in a photostationary state, where the reaction solution contained both **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** and **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(X)** in an approximately 3 : 1 ratio, as described above. Fig. 8 illustrates the initial stage of photocatalytic CO formation at lower light intensity ( $3.2 \times 10^{-9}$  einstein s<sup>-1</sup>) than that used in the case of Fig. 2. An induction period of CO formation was observed in the case of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re**, which strongly indicates that **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(X)** played an important role in the photocatalytic reaction. Therefore, we synthesized **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(X)** by reacting **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(MeCN)**, TEOA, and CO<sub>2</sub><sup>11</sup> and investigated the photocatalytic ability of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(X)**; the results are also shown in Fig. 8 (green). The clear induction period of CO formation disappeared; however, the quantum yield of CO formation ( $\Phi_{\text{CO}} = 0.12$ ) was lower than that achieved with **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** ( $\Phi_{\text{CO}} = 0.18$ , red in Fig. 8). Given these results, we examined the photocatalytic ability of a 3 : 1 mixed system of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** and **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(X)**, which is a similar ratio observed in the photostationary state when only **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** was used as the photocatalyst (Fig. 6). As shown in Fig. 8 (orange), no clear induction period

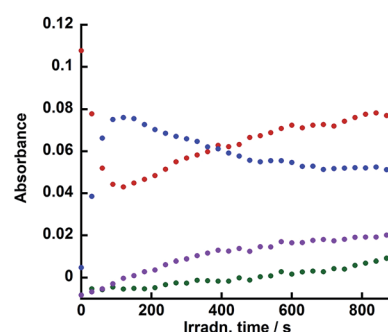
was observed and the quantum yield of CO formation achieved using this system ( $\Phi_{\text{CO}} = 0.19$ ) was similar to that achieved using **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** after the induction period ( $\Phi_{\text{CO}} = 0.18$ ). Therefore, we conclude that **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** and **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(X)** played important but different roles in the photocatalytic reaction.

Fig. 9 illustrates the rise and decay curves of the FT-IR absorption peaks (Fig. 7) attributed to each diad in the reaction solution during irradiation. However, immediately after the irradiation was started, the OERs of the Re unit in **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** (blue) formed rapidly and its concentration decreased between 120 s and 600 s of irradiation time, the non-reduced **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** (red) was recovered. Further irradiation did not induce a change in the ratio between the OERs and non-reduced species. The decrease of the concentration of the OERs appeared to occur after **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(X)** (green and purple) was accumulated in the reaction solution. These results indicate that efficient electron transfer from the OERs of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** to **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(X)** and/or an intermediate produced from the OERs of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(X)** occurred during the steady-state CO formation in the photocatalytic reaction.

Scheme 1 summarizes the possible mechanism for the photocatalytic reaction involving **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re**. The Ru unit is selectively excited, and the resulting <sup>3</sup>MLCT excited state is reductively quenched by BNAH to give the OER species of the Ru unit of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re**. Rapid intramolecular electron transfer proceeds from the OERs of the Ru unit to the Re unit to give the OER species of the Re unit of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re**. Rapid abstraction of a proton from the one-electron-oxidized BNAH by TEOA and dimerization have been reported to proceed to give BNA<sub>2</sub>. In the first stage of the photocatalytic reaction, approximately a quarter of the added **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** was efficiently converted into **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(X)** (X = <sup>-</sup>OC<sub>2</sub>H<sub>4</sub>N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub> or <sup>-</sup>OC(O)OC<sub>2</sub>H<sub>4</sub>N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub>), which was the real photocatalyst for CO<sub>2</sub> reduction. **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re**, which remained in the solution, functioned as a redox photosensitizer that supplied electrons to **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(X)** and/or the intermediate during the photocatalytic reaction. Notably, the

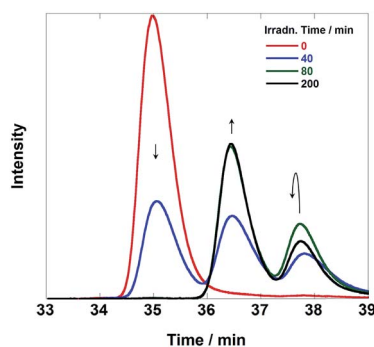


**Fig. 8** Photocatalytic CO formation using DMF-TEOA (5 : 1 v/v) solutions containing 0.1 M of BNAH and 0.3 mM of Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re (red), Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(X) (green), or a 3:1 mixture of Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re and Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(X) (orange). The reaction conditions were same as those described in Fig. 5.



**Fig. 9** Changes in the intensities of the absorbance peaks in the *in situ* IR spectra (Fig. 7): Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(X) (green, 2018 cm<sup>-1</sup>, X = <sup>-</sup>OC(O)OC<sub>2</sub>H<sub>4</sub>N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub>; purple, 2006 cm<sup>-1</sup>, X = <sup>-</sup>OC<sub>2</sub>H<sub>4</sub>N(C<sub>2</sub>-H<sub>4</sub>OH)<sub>2</sub>), Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re (red, 1938 cm<sup>-1</sup>), and the OER species of Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re (blue, 1909 cm<sup>-1</sup>). See Fig. 7.

As previously described, the durability of **Ru(CH<sub>2</sub>SCH<sub>2</sub>)Re** was much lower than that observed for the other diads. Fig. 10 shows SEC analysis data of the reaction solution; these chromatograms clearly indicate that **Ru(CH<sub>2</sub>SCH<sub>2</sub>)Re** completely disappeared after irradiation for 80 min and that two new species with smaller sizes formed. The LC-MS analysis data (Fig. S10, ESI<sup>†</sup>) indicated that the species detected at retention times of 36.5 min and 37.8 min were Ru(II) mononuclear complexes, *i.e.*, **Ru(CH<sub>2</sub>OCH<sub>2</sub>)**, **Ru**, and [Ru(dmb)<sub>2</sub>(CS<sup>-</sup>)]<sup>+</sup> (CS<sup>-</sup> = MebpyCH<sub>2</sub>S<sup>-</sup>), and Re(I) mononuclear complexes, *i.e.*, **Re**, [Re(CH<sub>2</sub>OCH<sub>2</sub>)(CO)<sub>2</sub>{P(*p*-FPh)<sub>3</sub>}<sub>2</sub>}]<sup>+</sup>, and [Re(dmb)(CO)<sub>2</sub>{P(*p*-FPh)<sub>3</sub>}(MeCN)]<sup>+</sup> (MeCN was contained in the eluent), respectively. Therefore, **Ru(CH<sub>2</sub>SCH<sub>2</sub>)Re** was completely cleaved to give the mononuclear complexes in the first stage of the reaction, which should lower both the efficiency and durability of the photocatalysis of **Ru(CH<sub>2</sub>SCH<sub>2</sub>)Re**.



**Fig. 10** Size exclusion chromatograms of the solutions before and after the photocatalytic reaction using  $\text{Ru}(\text{CH}_2\text{SCH}_2)\text{Re}$  (irradiation times: 0, 40, 80, and 200 min). The reaction and analytical conditions were the same as those described in Fig. 6.

## General procedures

UV-vis absorption spectra were recorded on a JASCO V-565 spectrophotometer.  $^1\text{H}$  NMR spectra were recorded on a JEOL AL300 (300 MHz) spectrometer. The residual proton of the deuterated solvent (acetone- $d_6$  or acetonitrile- $d_3$ ) was used as an internal standard. Emission spectra were measured at  $25 \pm 0.1$  °C under an Ar atmosphere using a JASCO FP-6500 spectrofluorometer. Emission quantum yields were obtained with a Hamamatsu photonics C-9920-02 integrating sphere and a multi-photodiode-array detector. Emission lifetimes were measured with a Horiba FluoroCube time-correlated single-photon counting system (the excitation source was an LED pulse lamp (456 nm) with an instrumental response time of less than 0.1 ns). In the quenching experiments, the changes in the emission intensities of solutions containing a complex were monitored in the presence of various amounts of the quencher, BNAH. Quenching rate constants ( $k_q$ ) were calculated from linear Stern–Volmer plots. Electrospray ionization-mass spectroscopy (ESI-MS) was recorded on a Shimadzu LCMS-2010A mass spectrometer using MeCN or MeOH as the mobile phase. The redox potentials of the complexes in a MeCN solution were measured using a cyclic voltammetric technique. The CVs were recorded on an ALS/CHI CHI-620 electrochemical analyzer using  $\text{Et}_4\text{NBF}_4$  (0.1 M) as the supporting electrolyte, a glassy-carbon disk working electrode (3 mm diameter), an  $\text{Ag}/\text{AgNO}_3$  (0.01 M) reference electrode, and a Pt counter electrode. The scan rate was  $200 \text{ mV s}^{-1}$ . Analytical SEC<sup>12</sup> was conducted using an HPLC system consisting of a JASCO 880-PU pump, a pair of Shodex PROTEIN KW402.5 columns, a KW-LG guard column, a Rheodyne 7125 injector, and a JASCO MD-2010 plus UV-Vis photodiode-array detector. The column temperature was maintained at 40 °C using a JASCO 860-CO column oven. A mixed solution of MeCN–MeOH (1 : 1 v/v) containing  $\text{CH}_3\text{COONH}_4$  (0.5 mM) was used as the mobile phase. In the case of HPLC(SEC)-MS analyses, a HPLC system consisting of the SEC columns and the guard column, a Rheodyne 7125 injector, a Shimadzu FCV-10ALVP gradient unit, and a Shimadzu LC-10ADVP pump was connected before the ESI-MS detector. The column temperature was maintained at 40 °C using a Shimadzu SPD CTO-10ACVP oven. A MeCN–MeOH (1 : 1 v/v) mixed solution containing  $\text{CH}_3\text{COONH}_4$  (0.05 mM) was used as the mobile phase. Isolation of the diads was achieved by preparative SEC using a pair of Shodex PROTEIN KW 2002.5 columns, a KW-LG guard column, and a JAI LC-9201 recycling preparative HPLC apparatus with a JASCO 870-UV detector. A MeCN–MeOH (1 : 1 v/v) mixed solution containing  $\text{CH}_3\text{COONH}_4$  (0.15 mM) was used as the mobile phase.

## Photocatalytic reactions

Photocatalytic reactions were performed on a 4 mL DMF-TEOA (5 : 1 v/v) mixed solution containing the diad (0.05 mM) and BNAH (0.1 M) in an 11 mL test tube (i.d. 8 mm). After the solution was purged with CO<sub>2</sub> for 15 min, it was irradiated in a





Yield 19%. Elemental analysis calcd (%) for  $\text{C}_{86}\text{H}_{72}\text{F}_{24}\text{N}_8\text{O}_3\text{-P}_5\text{ReRuS}$ : C. 47.04; H. 3.31; N. 5.10; S. 1.46. Found: C. 47.04; H. 3.45; N. 5.09; S. 1.68.  $^1\text{H-NMR}$  (300 MHz, acetone- $d_6$ )  $\delta$ /ppm: 8.76 (s, 1H,  $\gamma$ -bpy-3), 8.66 (s, 5H,  $\beta$ -bpy-3, dmb-3), 8.33 (s, 1H,  $\delta$ -bpy-3), 8.26 (s, 1H,  $\alpha$ -bpy-3), 8.11 (d,  $J = 5.6$  Hz, 1H,  $\gamma$ -bpy-6), 7.96 (d,  $J = 5.6$  Hz, 1H,  $\beta$ -bpy-6), 7.89–7.81 (m, 6H,  $\alpha$ -bpy-6, dmb-6,  $\delta$ -bpy-6), 7.53 (d,  $J = 6.0$  Hz, 1H,  $\beta$ -bpy-5), 7.39–7.29 (m, 17H,  $\alpha$ -bpy-5, dmb-5, Ph-*o*), 7.17 (d,  $J = 5.6$  Hz, 1H,  $\gamma$ -bpy-5), 7.10 (dd,  $J_{\text{HH}} = 8.6$  Hz,  $J_{\text{FH}} = 8.4$  Hz, 12H, Ph-*m*), 6.99 (d,  $J = 5.6$  Hz, 1H,  $\delta$ -bpy-5), 3.94–3.88 (m, 4H,  $\beta$ -CH<sub>2</sub>,  $\gamma$ -CH<sub>2</sub>), 2.57–2.54 (m, 18H, dmb-CH<sub>3</sub>,  $\alpha$ -bpy-CH<sub>3</sub>,  $\delta$ -bpy-CH<sub>3</sub>). FT-IR (in CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{\text{CO}}$ /cm<sup>-1</sup>: 1868, 1939. ESI-MS (eluent: MeCN)  $m/z$ : 581 ( $[\text{M} - 3\text{PF}_6^-]^{3+}$ ), 944 ( $[\text{M} - 2\text{PF}_6^-]^{2+}$ ).

[(dmb)<sub>2</sub>Ru(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Re{P(*p*-FPh)<sub>3</sub>}<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub> (Ru(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Re). Yield 72%. Elemental analysis calcd (%) for C<sub>87</sub>H<sub>72</sub>F<sub>24</sub>N<sub>8</sub>O<sub>2</sub>P<sub>5</sub>ReRu: C. 48.38; H. 3.36; N. 5.19. Found: C. 48.40; H. 3.45; N. 5.06. <sup>1</sup>H-NMR (300 MHz, acetone-*d*<sub>6</sub>) δ/ppm: 8.61 (s, 1H, β-bpy-3), 8.59 (s, 5H, α-bpy-3, dmb-3), 8.19 (s, 1H, γ-bpy-3), 8.16 (s, 1H, δ-bpy-3), 7.98 (d, *J* = 5.3 Hz, 1H, γ-bpy-6), 7.80–7.78 (m, 2H, β-bpy-6, α-bpy-6), 7.74–7.72 (m, 5H, δ-bpy-6, dmb-6), 7.38 (d, *J* = 6.0 Hz, 1H, β-bpy-5), 7.32–7.25 (m, 17H, α-bpy-5, dmb-5, Ph-*o*), 7.04 (dd, *J*<sub>HH</sub> = 8.6 Hz, *J*<sub>FH</sub> = 8.6 Hz, 12H, Ph-*m*), 6.96 (d, *J* = 5.6 Hz, 1H, γ-bpy-5), 6.90 (d, *J* = 5.9 Hz, 1H, δ-bpy-5), 2.86 (s, 2H, β-CH<sub>2</sub>), 2.78 (s, 2H, γ-CH<sub>2</sub>), 2.50–2.40 (m, 18H, dmb-CH<sub>3</sub> α-bpy-CH<sub>3</sub>, δ-bpy-CH<sub>3</sub>), 2.01 (tt, 4H, *J* = 2.1 Hz, 2.1 Hz, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-). FT-IR (in CH<sub>2</sub>Cl<sub>2</sub>) ν<sub>CO</sub>/cm<sup>-1</sup>: 1868, 1938. ESI-MS (eluent: MeCN) *m/z*: 575 ([M - 3PF<sub>6</sub>]<sup>-3+</sup>), 935 ([M - 2PF<sub>6</sub>]<sup>-2+</sup>).

mL), and the solution was refluxed for 5 h under an N<sub>2</sub> atmosphere in the absence of light. After evaporation of the solvent, **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>Br** was isolated by ion-exchange column chromatography on a SP Sephadex C-25 column using acetonitrile–water (1 : 1 v/v) containing NH<sub>4</sub>PF<sub>6</sub> as the eluent. Although a small amount of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(MeCN)** byproduct was present as a contaminant, the recovered sample was used in the subsequent synthesis without further purification. Yield: 66.5 mg (crude). FT-IR (in CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{\text{CO}}$ /cm<sup>-1</sup>: 2039, 2022, 1919. ESI-MS (eluent: MeCN)  $m/z$ : 600 ([M – 2PF<sub>6</sub>]<sup>-2+</sup>).

**Synthesis of [(dmb)<sub>2</sub>Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(MeCN)](PF<sub>6</sub>)<sub>3</sub>·H<sub>2</sub>O (Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(MeCN)).** The crude sample (75.3 mg) of Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>Br containing Ru(CH<sub>2</sub>OCH<sub>2</sub>)-Re(CO)<sub>3</sub>(MeCN) and CF<sub>3</sub>SO<sub>3</sub>H (0.03 mL, 0.34 mmol) were dissolved in *o*-dichlorobenzene (7 mL), and the solution was refluxed for 5 h under an Ar atmosphere in the absence of light. After evaporation of the solvent, the product was isolated by ion-exchange column chromatography on a CM Sephadex C-25 column using MeCN-H<sub>2</sub>O (1 : 1 v/v) containing NH<sub>4</sub>PF<sub>6</sub> as the eluent. After evaporation of the solvent, Ru(CH<sub>2</sub>OCH<sub>2</sub>)-Re(CO)<sub>3</sub>(MeCN) was obtained by recrystallization from a CH<sub>2</sub>Cl<sub>2</sub>-diethyl ether mixed solution as a red solid. The yield was 70% (56.5 mg, 0.05 mmol). Elemental analysis calcd (%) for C<sub>53</sub>H<sub>51</sub>F<sub>18</sub>N<sub>9</sub>O<sub>5</sub>P<sub>3</sub>ReRu: C, 39.39; H, 3.18; N, 7.80. Found: C, 39.36; H, 3.19; N, 7.71. <sup>1</sup>H-NMR (300 MHz, acetonitrile-*d*<sub>3</sub>) δ/ppm: 8.96 (d, *J* = 5.9 Hz, 1H, β-bpy-6), 8.85 (d, *J* = 5.7 Hz, 1H, α-bpy-6), 8.47 (s, 1H, β-bpy-3), 8.44 (s, 1H, α-bpy-3), 8.37 (s, 1H, γ-bpy-3), 8.34 (s, 1H, δ-bpy-3), 8.32 (s, 4H, dmb-3), 7.70 (d, *J* = 5.7 Hz, 1H, γ-bpy-6), 7.68 (d, *J* = 6.2 Hz, 1H, β-bpy-5), 7.55–7.49 (m, 6H, δ-bpy-6, dmb-6, α-bpy-5), 7.39 (d, *J* = 5.7 Hz, 1H, γ-bpy-5), 7.21–7.20 (m, 5H, δ-bpy-5, dmb-5), 4.91 (s, 2H, β-CH<sub>2</sub>), 4.88 (s, 2H, γ-CH<sub>2</sub>), 2.56–2.51 (m, 18H, dmb-CH<sub>3</sub>, β-bpy-CH<sub>3</sub>, γ-bpy-CH<sub>3</sub>), 2.04 (s, 3H, CH<sub>3</sub>-CN-). FT-IR (in MeCN) ν<sub>CO</sub>/cm<sup>-1</sup>: 2039, 1934. ESI-MS (eluent: MeCN) *m/z*: 600 ([M - MeCN + Br<sup>-</sup> - 3PF<sub>6</sub><sup>-</sup>]<sup>3+</sup>), 655 ([M - 2PF<sub>6</sub><sup>-</sup>]<sup>2+</sup>).

**Synthesis of** [(dmb)<sub>2</sub>Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(OC(O)OC<sub>2</sub>H<sub>4</sub>-N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub>)](PF<sub>6</sub>)<sub>2</sub> (Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(X)). Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(MeCN) was dissolved in DMF, and the resulting solution was stirred overnight. TEOA was added to the solution, and the solution was stirred for an hour to give a mixture of Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(DMF) and Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(TEOA). Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(X) was obtained by bubbling the solution with CO<sub>2</sub> for 10 min. The reversibility of this CO<sub>2</sub> insertion reaction was confirmed by the recovery of the starting complexes in the solution after bubbling with Ar for 20 min. FT-IR (in MeCN)  $\nu_{\text{CO}}$ /cm<sup>-1</sup>: 2006, 2018 (Fig. S5, ESI<sup>†</sup>).

The greatest photocatalytic activity for CO<sub>2</sub> reduction using BNAH as the reductant was achieved using **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** ( $\Phi_{\text{CO}} = 0.18$ ,  $\text{TON}_{\text{CO}} = 253$ ). Introduction of an oxygen atom into the bridging unit improved the oxidation power of the excited Ru unit in the diad and increased the driving force of the intramolecular electron transfer from the OER species of the Ru unit to the Re unit. During the photocatalytic reaction, a part of the used **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** was converted into

**Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(X)** (X = <sup>−</sup>OC<sub>2</sub>H<sub>4</sub>N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub> or <sup>−</sup>OC(O)-OC<sub>2</sub>H<sub>4</sub>N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub>) during the initial stage of the photocatalytic reaction. The 3 : 1 mixture of **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re** and **Ru(CH<sub>2</sub>OCH<sub>2</sub>)Re(CO)<sub>3</sub>(X)**, which respectively functioned as a photosensitizer and a photocatalyst in the photostationary state, efficiently photocatalyzed CO<sub>2</sub> reduction for an extended period.

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